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G. Koch, F. Baumgärtner, H. Goldacker,
W. Ochsenfeld, H. Schmieder
Institut für Heiße Chemie
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H. Schmieder

Gesellschaft für Kernforschung m.b.H., Karlsruhe

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Abstract

In 1974 a "Mark I" solvent extraction flowsheet for a German large-scale LWR fuel reprocessing plant has been designed under the guidance of Gesellschaft für Kernforschung (GfK). Since then, several improved procedures have been developed, and have step by step been adopted into the original flowsheet. In preparing the GfK flowsheet, specific attention has been paid to safety and reliability of operation, to the minimization of liquid medium-level wastes, and to the minimization of environmental releases. This paper discusses several of the specific features of the present version of the GfK flowsheet.

Zusammenfassung

Ein PUREX-Extraktionsfließschema für eine große LWR-Brennstoff-Wiederaufarbeitungsanlage

1974 wurde unter Federführung der Gesellschaft für Kernforschung ein "Mark I"-Extraktionsfließschema für eine große deutsche LWR-Brennstoff-Aufarbeitungsanlage erstellt. In der Zwischenzeit wurde eine Reihe von verbesserten Verfahrensschritten entwickelt und in das ursprüngliche Fließschema übernommen. Bei der Ausarbeitung des GfK-Extraktionsfließschemas wurde insbesondere auf eine hohe betriebliche Verfügbarkeit, auf die weitgehende Reduzierung flüssiger mittelaktiver Abfälle, sowie auf eine Minimierung der Umweltbelastung Rücksicht genommen. In diesem Bericht werden verschiedene spezifische Verfahrensschritte der gegenwärtigen Version des GfK-Fließschemas diskutiert.

1. General Block Diagram

Fig. 1 presents a block diagram of the solvent extraction part of the flowsheet. Three extraction cycles are needed to obtain sufficient purification of the two product elements from fission products, which requires a decontamination factor (DF) of ca. $2 \cdot 10^7$. The U/Pu separation has been placed into the first extraction cycle, as a consequence of the criticality control concept foreseen for the original "Mark I" flowsheet which was based on homogeneous poisoning, by gadolinium nitrate, of equipment containing U+Pu. Minimization of Gd consumption, and the required decontamination of products from the neutron poison (DF between 10^4 and 10^5), both required that the U/Pu separation be placed into the first extraction cycle(1,2). Although the present GfK flowsheet does no longer foresee homogeneous poisoning by dissolved $Gd(NO_3)_3$, but instead proposes heterogeneous poisoning of equipment containing U+Pu by use of the new construction material, hafnium(3), the U/Pu separation has been maintained in the first extraction cycle, with the aim of minimizing the equipment fabricated from (expensive) hafnium, and of providing optimum purification efficiency of the process, in particular with regard to decontamination of U from Np(4) and Pu.

2. First Extraction Cycle

Fig. 2 presents a flow scheme of the first extraction cycle. It comprises six sieve-plate pulsed columns: extraction-scrub (HA), scrub (HS), tritium scrub (TS), plutonium backwash by electro-reduction (1BX), uranium scrub (1BS), and uranium backwash (1C). In addition, one mixer-settler for solvent clean-up (1CS) is included.

2.1 The HA-HS-TS Column System

The extraction-scrub system shows two unusual features. The first is the high solvent loading which amounts to 99 g U+Pu/l in the HAP stream, corresponding to >75 % of the maximum loading(1,2). In addition, a relatively high acidity, slightly in excess of 3 moles HNO_3/l aqueous phase, is maintained over the whole length of the HA column. Most of the published flowsheets(5) apply $\lesssim 65$ % loading, exceptions being the Marcoule flowsheet (100 g U/l in HAP)(6) and the USSR flowsheet (80 g U/l in HAP with 25 v/o TBP)(7). We propose an increased loading on the basis of our experience(1,8,9) that the formation of radiolytic cruds, which may lead to severe operational problems in the HA extractor (in particular with mixer-settlers)(10), can be suppressed to non-critical limits by applying a high solvent loading in combination with a high acidity in the HA contactor. This effect has been demonstrated in the MILLI experimental facility at Karlsruhe both with LWR fuels (burn-up up to 37000 MWd/t, cooling time down to 200 days) and with SBR fuel (burn-up 61000 MWd/t)(8,9,11). Solvent loadings up to 110 g U+Pu/l have been used in the MILLI without operational problems. An explanation of the effect may be offered by the observation(12) that the solubility of insoluble Zr-dibutylphosphate compounds, which form a major constituent of the cruds, both in the aqueous and in the organic phase increases with increasing acidity and uranium concentration, while at the same time the formation rate of these compounds drastically decreases.

The second specific feature is based on a proposal of the French C.E.A., and consists of the inclusion, after the HA and HS "double scrub" system, of an additional scrub column (TS) which serves for elimination of tritiated water from the organic solvent(13,14). The TSS solution is made up from non-tritiated water and acid (either fresh or recycled from later extraction cycles), and the tritiated water and acid dissolved or entrained in the organic solvent are exchanged against non-tritiated species. Thus the tritium is prevented from "smearing" over the equipment beyond the TS contactor, and is concentrated in the aqueous streams of the dissolver, HAW evaporator, 1WW tank, and HA-HS-TS column systems. By making use of extensive recycle of these tritiated streams, i.e. by using recovered tritiated water and acid for the dissolver acid, feed make-up, and HAS and HSS streams, the amount of tritiated waste water can be kept to a minimum, i.e. distinctly below 1 m^3 T-water per ton of fuel(15). Flow ratios aqueous : organic in the TS column (i.e. TSS : TSP) between 1 : 50 and 1 : 100 have been considered but a less extreme ratio of between 1 : 20 and 1 : 30 may be used without essential increase of the specific amount of tritiated waste water(14). With such a ratio, about 4 theoretical extraction stages are needed to keep the amount of tritium escaping with the TSP solution below 1 % of the input-tritium(14).

2.2 The 1BX-1BS-1C Column System

For U/Pu partitioning in the 1BX-1BS columns, use of the electrolytic in-line reduction process developed by GfK(16,17) is proposed. The 1BX column is very similar to a "normal" pulsed sieve-plate column. In our most recent design, the sieve-plates which are fabricated from titanium act as the cathodes, while the anode is formed by a central tube fabricated from platinized tantalum. The sieve-plates are fixed to the outer column tubing which is also fabricated from titanium, thus increasing the cathode area, while the electric insulation between the sieve-plates and the central anode tube is provided by ceramic annuli. Thus there is no separation between cathode and anode compartment as was provided in earlier designs(17). The column is run with the aqueous as the continuous phase. The only chemical addition to the system is the hydrazine nitrate introduced with the 1BXX stream which serves as a nitrous acid scavenger. Extractable Pu^{IV} and Pu^{VI} is cathodically reduced to inextractable Pu^{III}, and a sufficient excess of U^{IV} is cathodically formed to build a "barrier" against the break-through of non-reduced plutonium with the organic 1BXU stream. The particular advantage of the process, as compared against chemical reduction with ferrous sulfamate or with uranium(IV) nitrate / hydrazine nitrate, is that a fast and direct control is possible by regulation of the electric current supplied. Moreover, a high plutonium product concentration can be produced (GfK flowsheet: ca. 10 g/l Pu in 1BSP), the residual enrichment of the uranium remains unchanged, and the 1BSP solution contains no salt burden or corrosive reagents. The separation efficiency is similar to that of the U^{IV} partitioning process, with DF(U/Pu) and DF(Pu/U) values routinely between 1000 and 3000. Hot tests of the process, using an electrolytic mixer-settler, have been performed with good success in the MILLI facility, with FBR fuel of 61000 MWd/t burn-up and 15 % PuO_2 content(8).

Backwash of U in the 1C column is performed in the usual way, with 0,01 molar HNO_3 at 60°C.

2.3 The 1CS Contactor

For clean-up of the spent solvent a "salt-free" process recently developed at GfK Karlsruhe(15,18,19) is proposed. A hydrazine-hydrazine carbonate solution is applied for the removal of di- and monobutyl phosphoric acids and of fission products from the solvent. The washing efficiency is similar as with the "classic" Na_2CO_3/NaOH wash solution. A phase ratio aqueous : organic of about 1 : 20 is applied. Due to the slow kinetiks of the washing process(18), a mixer-settler with internal recycle (Holley-Mott type) is proposed as the 1CS contactor. The spent wash solution (1CSW) is mainly composed of hydrazine nitrate; the hydrazine can be decomposed into N_2 and H_2O by continuous electrooxidation(15,19), and the resulting MAW which is essentially salt-free can be concentrated by evaporation to a very small volume, which can be added to the high-level waste without essential increase of the 1WW volume.

By this way a major part of the medium-active liquid waste, together with its need for separate solidification and storage, can be eliminated.

The washed solvent still contains a variety of so-called "non-removable", high-molecular-weight radiolysis products which tend to form stable complexes with, e.g., Pu and Zr(20,21).
Although the formation rate of these products is low, they accumulate in the solvent and may finally limit the applicability of the solvent.

Removal of these "non-removable" products is possible by oxidative breakdown with lead dioxide. For this reason, a partial stream of the washed solvent can be led through a fixed-bed PbO_2-SiO_2 column, before recycle of the solvent to the process.

3. Uranium Purification Cycles

Fig. 3 presents a flow scheme of the two uranium purification cycles. Each cycle is equipped with two extraction columns (extraction - back extraction system) and one Holley-Mott type mixer-settler for solvent wash (hydrazine carbonate process). Specific features of this system are as follows:

1) A "dilute" flowsheet, with no intercycle evaporation, is proposed for the 2nd and 3rd uranium cycles. The feeds to these cycles (2DF and 3DF) are directly made up from the uranium product solutions of the preceding cycles by addition of concentrated nitric acid, to yield concentrations of ca. 75 g U/l and 1 mole HNO_3/l. Organic uranium concentrations of ca. 80 g U/l in 2DU and 3DU are obtained with 3 to 4 theoretical stages. The main reason for proposing this flowsheet lies in the fact that two intercycle evaporators, together with their auxiliary equipment (kerosene wash of the evaporator feed, etc.),

are saved(1). Regarding product purity, comparisons between a "dilute" and a "concentrated" flowsheet made in the MILLI yielded similar product purities in both cases; while the fission product DF values were the same, the DF(Pu) was slightly lower and the DF(Np) higher for the "dilute" flowsheet. Uranium product specifications are met with both types of flowsheet.

2) For removal of residual plutonium, some U^{IV} nitrate plus hydrazine nitrate is introduced with the 2DS stream in the upper stages of the 2D column. This measure serves at the same time for improved removal of Np since highly extractable Np^{VI} is reduced to less extractable lower valency states, and since HNO_2 (catalyst for oxidation of Np^V to Np^{VI}) is scavenged over the whole length of the column by hydrazine. Tests of the second cycle flowsheet in the MILLI yielded DF values between $3 \cdot 10^2$ and $1 \cdot 10^3$ for Pu and between 10 and 200 for Np(4,11).

3) Final purification from Np is carried out in the 3D column by maintaining a sufficiently high nitrous acid concentration over the whole length of the column, which leads to formation of inextractable Np^V. HNO_2 is best introduced as liquid N_2O_4 into the lower part of the 3D column (3DN stream in fig. 3). Due to the high extractability of HNO_2 by TBP(22), the nitrous acid is distributed over the whole 3D column. Alternately, HNO_2 may be introduced into the 3D column with the solvent stream (pretreatment of the 3DX stream with e.g. NO_2) or in the form of $NaNO_2$; however, the latter would lead to a salt-containing 3DW stream and is not recommended. Tests of the third cycle flowsheet in the MILLI yielded DF(Np) values between 70 and 1000(4).

4. Plutonium Purification Cycles

Fig. 4 presents a flow-scheme of the second plutonium purification cycle. The third plutonium cycle is essentially a repetition of the second cycle, and is for reasons of simplicity not depicted. Specific features of the plutonium purification cycles are as follows:

1) The product stream of the preceding cycle (1BSP or 2BP, respectively) is cleaned from dissolved or entrained organic material (in particular, TBP and HDBP) by washing with n-alkane in the 1PW (or 2PW, respectively) column. Alternately, a recently developed process using a fixed-bed column with a solid sorbent, Lewapol®, may be used for TBP-HDBP removal from the solution(9).

2) In the product solution from the 1PW (or 2PW) column, most of the plutonium is threevalent, and the solution contains excess hydrazine. Re-oxidation of Pu^{III} to extractable Pu^{IV}, and removal of $N_2H_5^+$, is carried out by continuous in-line electro-oxidation in the 2EO (or 3EO) oxidation cell(17,19). The process has been optimized to yield essentially pure Pu^{IV} solutions, with Pu^{VI} below 2 % of the total Pu. The product solutions from this process are made up to flowsheet conditions with HNO_3, and are fed as feed streams (2AF or 3AF) to the 2A or 3A columns.

3) Backwash of the plutonium in the 2B (or 3B) column is carried out by in-line electro-reduction to Pu^{III} (17). This process yields significantly higher Pu concentrations in the 2BP or 3BP product streams than can be obtained with non-reductive plutonium stripping (GfK flowsheet: 30 g Pu/l in 2BP, 60 g Pu/l in 3BP).

4) Similar to the uranium purification system, each of the two plutonium cycles includes a separate solvent wash system (2BS or 3BS, respectively). Again the "salt-free" hydrazine-hydrazine carbonat process (15,18,19) is applied. Residual uranium which is carried with the 2BW or 3BW streams is also re-extracted in the solvent wash systems.

List of Figures

Fig. 1 Block diagram of solvent extraction flowsheet

Fig. 2 Flow scheme of the first extraction cycle. ↯ designates in-line electro-reduction. TBP designates 30 v/o TBP / n-alkane (mixture C_{10} - C_{13}). Interim tanks are not shown.

Fig. 3 Flow scheme of the uranium purification cycles. TBP designates 30 v/o TBP / n-alkane (mixture C_{10} - C_{13}). Interim tanks not shown.

Fig. 4 Flow scheme of the second plutonium purification cycle. Interim tanks not shown. ↯ designates in-line electro-oxidation or in-line electro-reduction. TBP designates 30 v/o TBP / n-alkane (mixture C_{10} - C_{13}). The third plutonium purification cycle is essentially a repetition of the 2nd cycle.

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Fig. 1

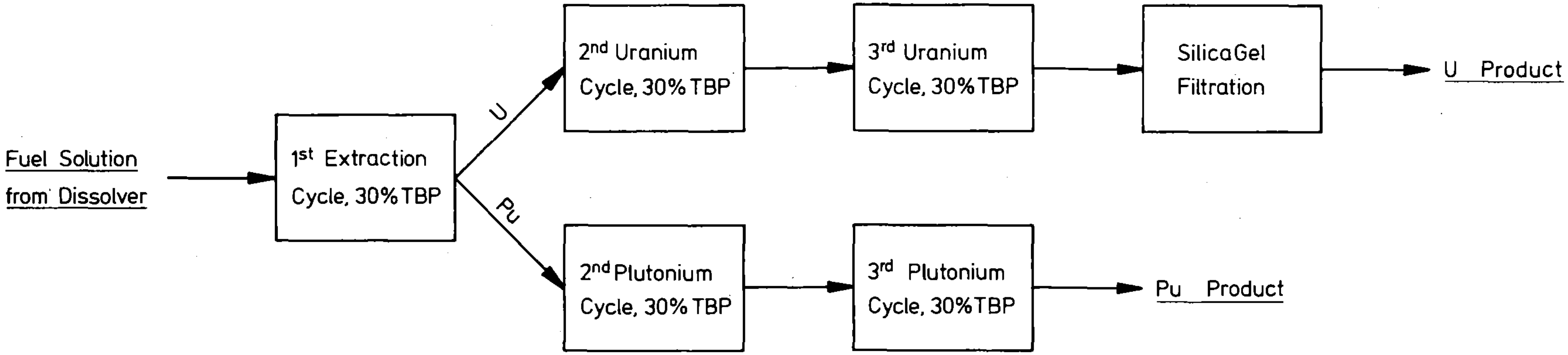

Fuel Solution from Dissolver
1st Extraction Cycle, 30% TBP
U
Pu
2nd Uranium Cycle, 30% TBP
3rd Uranium Cycle, 30% TBP
SilicaGel Filtration
U Product
2nd Plutonium Cycle, 30% TBP
3rd Plutonium Cycle, 30% TBP
Pu Product

Fig. 2

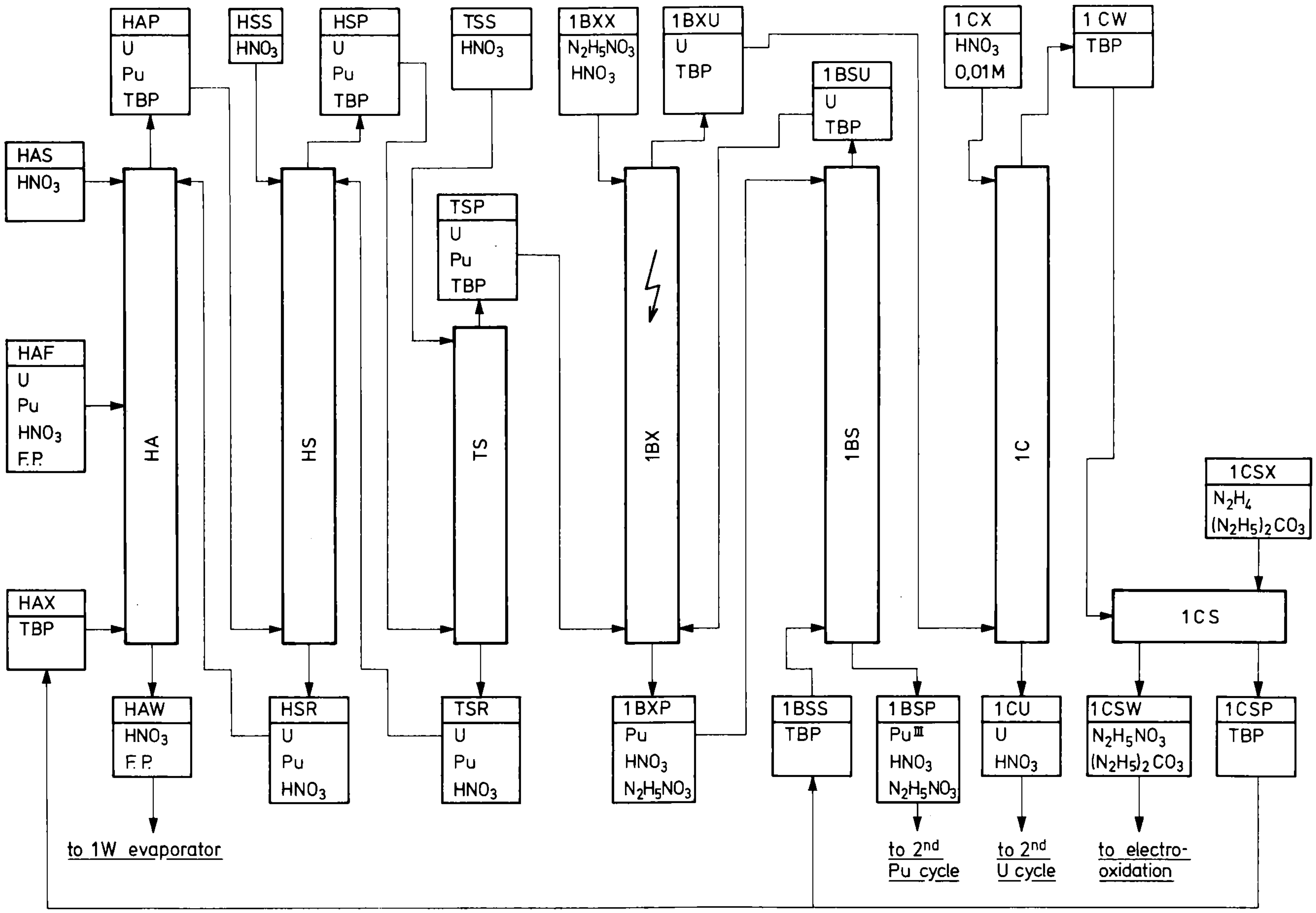

HAP
U
Pu
TBP
HSS
HNO_3
HSP
U
Pu
TBP
TSS
HNO_3
1BXX
$N_2H_5NO_3$
HNO_3
1BXU
U
TBP
1BSU
U
TBP
1CX
HNO_3
0,01M
1CW
TBP
HAS
HNO_3
TSP
U
Pu
TBP
HAF
U
Pu
HNO_3
F.P.
HA
HS
TS
1BX
1BS
1C
1CSX
N_2H_4
$(N_2H_5)_2CO_3$
HAX
TBP
1CS
HAW
HNO_3
F.P.
HSR
U
Pu
HNO_3
TSR
U
Pu
HNO_3
1BXP
Pu
HNO_3
$N_2H_5NO_3$
1BSS
TBP
1BSP
Pu^{III}
HNO_3
$N_2H_5NO_3$
1CU
U
HNO_3
1CSW
$N_2H_5NO_3$
$(N_2H_5)_2CO_3$
1CSP
TBP
to 1W evaporator
to 2nd Pu cycle
to 2nd U cycle
to electro-oxidation

Fig. 3

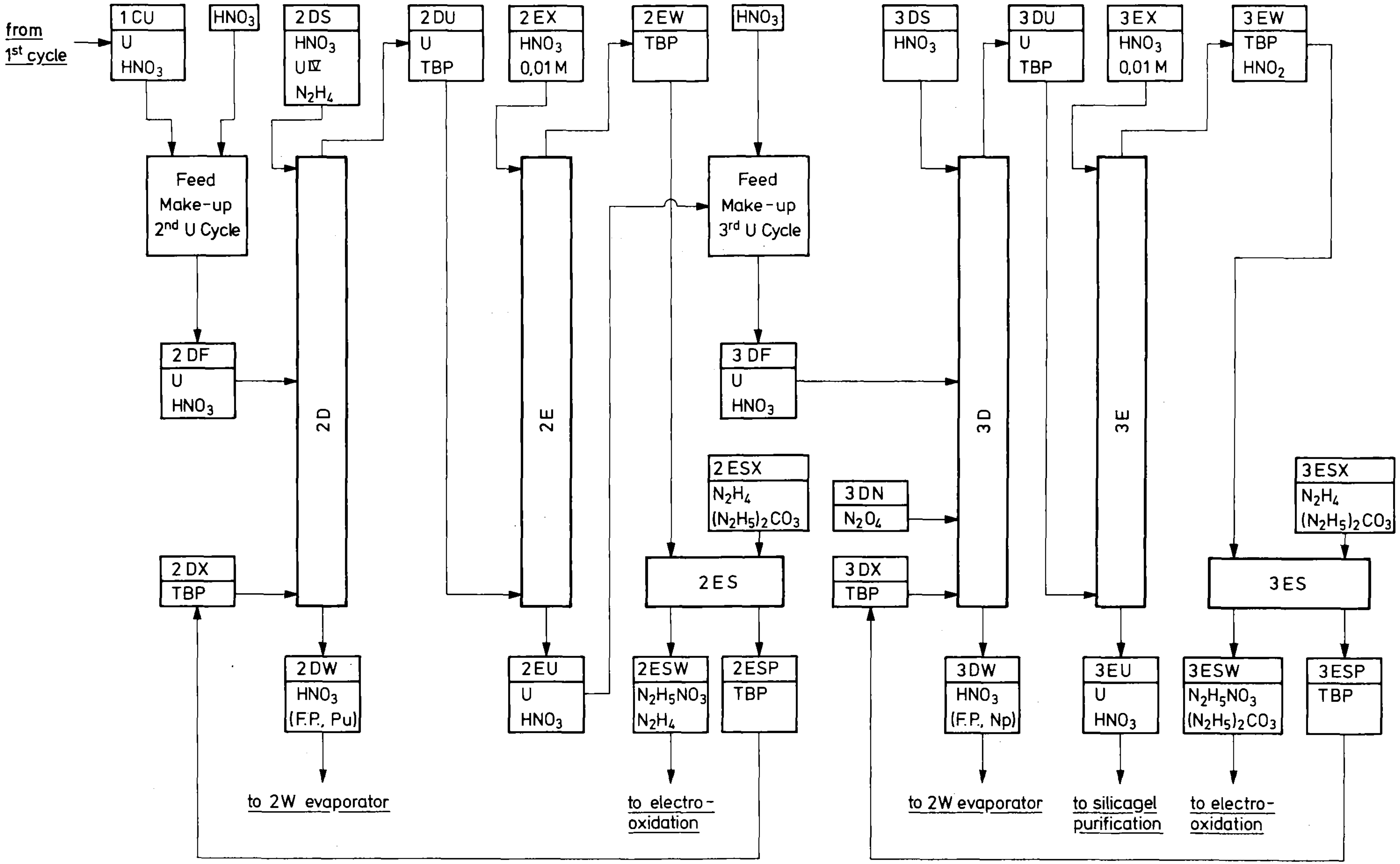
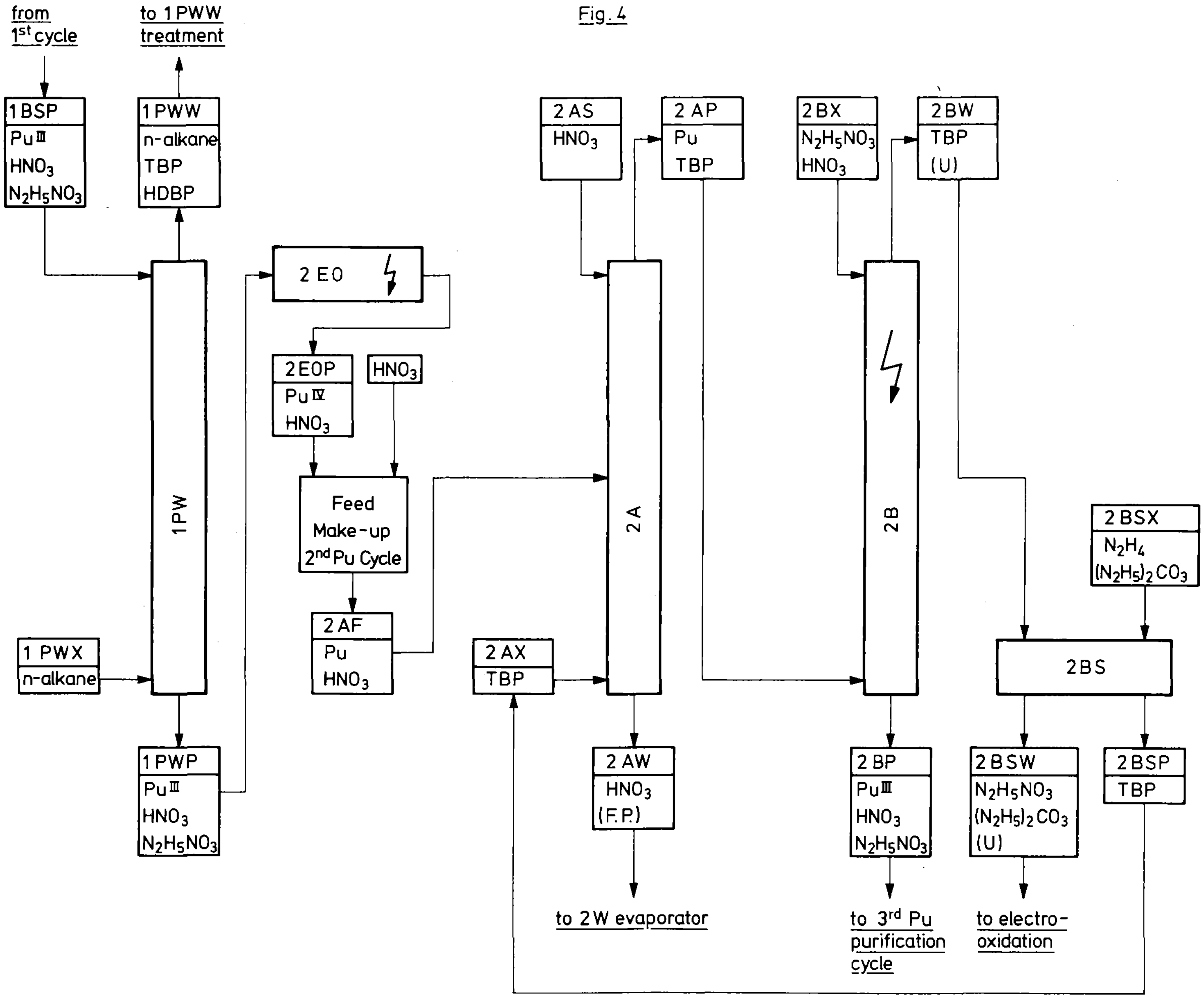

from 1st cycle
1 CU
U
HNO_3
HNO_3
2 DS
HNO_3
U IV
N_2H_4
2 DU
U
TBP
2 EX
HNO_3
0,01 M
2 EW
TBP
HNO_3
3 DS
HNO_3
3 DU
U
TBP
3 EX
HNO_3
0,01 M
3 EW
TBP
HNO_2
Feed Make-up 2nd U Cycle
Feed Make-up 3rd U Cycle
2 DF
U
HNO_3
2D
2E
3 DF
U
HNO_3
3D
3E
2 ESX
N_2H_4
$(N_2H_5)_2CO_3$
3 DN
N_2O_4
3 ESX
N_2H_4
$(N_2H_5)_2CO_3$
2 DX
TBP
2 ES
3 DX
TBP
3 ES
2 DW
HNO_3
(F.P., Pu)
2 EU
U
HNO_3
2 ESW
$N_2H_5NO_3$
N_2H_4
2 ESP
TBP
3 DW
HNO_3
(F.P., Np)
3 EU
U
HNO_3
3 ESW
$N_2H_5NO_3$
$(N_2H_5)_2CO_3$
3 ESP
TBP
to 2W evaporator
to electro-oxidation
to 2W evaporator
to silicagel purification
to electro-oxidation

Fig. 4


from 1st cycle
to 1 PWW treatment
1 BSP
Pu III
HNO3
N2H5NO3
1 PWW
n-alkane
TBP
HDBP
1 PW
1 PWX
n-alkane
1 PWP
Pu III
HNO3
N2H5NO3
2 EO
2 EOP
Pu IV
HNO3
HNO3
Feed Make-up 2nd Pu Cycle
2 AF
Pu
HNO3
2 AS
HNO3
2 AP
Pu
TBP
2 A
2 AX
TBP
2 AW
HNO3
(F.P.)
to 2 W evaporator
2 BX
N2H5NO3
HNO3
2 BW
TBP
(U)
2 B
2 BSX
N2H4
(N2H5)2 CO3
2 BS
2 BP
Pu III
HNO3
N2H5NO3
to 3rd Pu purification cycle
2 BSW
N2H5NO3
(N2H5)2 CO3
(U)
to electro-oxidation
2 BSP
TBP